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Reliability testing of nano-particle system packaging

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Abstract Metal nanoparticle applications in nanoelectronics are based on single nanodots or 1-D nanodot chains (both for single electron transistors), or 2-D discontinuous metal thin film (DMTF) arrays (e.g. for sensors), or 3-D polymer or ceramic "cermets," (for high resistivity resistors and high-*k* dielectrics). DMTF fabrication relies upon weak substrate adhesion for discrete island formation, which promotes long-term instability and reliability problems. Past work on DMTF nanodot stability is applicable to future nanoelectronics and nanopackaging.

1 Introduction

Discontinuous metal thin film (DMTF) nanodot arrays consist of multiple metal islands separated by tunneling gaps. The typical dimensions of interest are nm for both island sizes (say 1–10 nm in diameter), and gaps (say typically 2 nm). These arrays can represent the tunneling junctions of single-electron transistors (SETs) or other potential nanoelectronic devices based on nanodots or electron-tunneling, with the dimensions including those necessary for room temperature (or liquid nitrogen) SET operation. DMTF structures have been studied in the past, and a number of causes of instabilities in their electrical properties have been documented (Morris et al. 2004a, b). The weak substrate interaction (e.g. for gold on glass), which promotes the formation of discrete nanodots, also leads to structural instability by various mechanisms,

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including nanodot island drift and coalescence, Ostwald ripening, and island shape changes by surface self-diffusion, etc. In addition, the application of an applied field can lead to shifts in electrical properties due to substrate polarization or ion drift. The purpose of this work is to anticipate potential reliability issues with packaged nanoelectronic devices, and nanopackaging applications of nanodot structures, and to report the beginning of a reliability research program in this area.

2 The nanodot coulomb block and discontinuous metal thin films

Metal nanoparticle applications are proliferating, in nanoelectronics, for example, in some single electron transistor (SET) configurations (Morris et al. 2004a, b), and in the applications of nanotechnology to microelectronics packaging (Morris 2008a, b; Wu and Morris 2008; Lu and Wong 2008). Nanoelectronics packaging (i.e. the packaging of novel nanoelectronics technologies), has tended to lag these areas (Morris 2008b). Some SET structures operate with only a single nanodot, while others use a 1-D line of dots, possibly through a regular or random 2-D DMTF array. The quantum automata variant uses a fournanodot unit cell. Packaging applications may employ DMTF structures, or more commonly the 3-D "cermet" variant, where the nanodots are encased in polymer or ceramic. Although simplified SET theory tacitly assumes spherical nanodots, the generalized ellipsoidal shape of the nanodot shown in Fig. 1 is the minimal energy configuration of a charged dot (Morris 1972a, Morris 1972b; Morris and Coutts 1977) on a surface, or can be a transient nonequilibrium form due to growth from a substrate adatom population (Morris 1975a). Electronic conduction between

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Fig. 1 The geometry of two ellipsoidal nanodots of eccentricity $e = (1 - (t/r)^2)^{1/2}$ (Morris and Coutts 1977)

contacts and dots, or between dots, distance *d* apart, is by tunneling (Morris 1972c; Morris and Coutts 1977; Wu and Morris 1998), with probability proportional to exp- $(2 m\Phi)^{1/2}(4\pi d/h)$, (where *m* is the electronic mass, Φ is the effective tunneling barrier height, and *h* is Planck's constant), and with an associated electrostatic activation energy, δE , (and for $\theta \approx 180^{\circ}$) at applied field E_a (Morris 1972a, c; Morris and Coutts 1977) and for p = d/R, R = 2r + d, with island eccentricity *e*:

$$\delta E = q^2 / C$$

= $(q^2 / 4\pi \varepsilon R) (2/e) [\sin^{-1}e - \sin^{-1}(e(1-p)/(1+p))] / (1-p) - qRE_a$

for

$$\begin{split} E_{\rm a} &< E_{\rm amin} = \left(q^2/4\pi\epsilon R\right) 4p(1+p)^{-1} \\ &\times \left[(1+p)^2 - e^2(1-p)^2 \right]^{-1/2}, \\ \delta E &= \left(q^2/4\pi\epsilon R\right)(2/e) \left[\sin^{-1}e - \sin^{-1}(e(1-p)R) \\ &/((1-p)R + 2x))\right] / (1-p) - qE_{\rm a}x/p \end{split}$$

where

$$\times \left\{ \left[\frac{\left[\left\{ 2qp/\pi \varepsilon E_{a}(1-p)^{2}R^{2}e^{2} \right\}^{2} + 1 \right]^{1/2} + 1}{2} \right]^{1/2} - e^{-1} \right\}$$

for

$$E_{\text{amin}} < E_{\text{a}} < E_{\text{amax}} = (q^2/4\pi\epsilon R)4p(1-p)^{-2}(1-e^2)^{-1/2},$$

and $\delta E = 0$ at $E_a = E_{amax}$, which corresponds to the 0°K coulomb block (SET) threshold condition. In a DMTF of N_0 nanodots, $N_0 \exp - \delta E/kT$ are randomly charged at any time, and a single coulomb block (SET) nanodot is charged exp $- \delta E/kT$ of the time, washing out the abrupt threshold at finite *T* (Morris 2006).

A great deal of past experimental work on the stability of nanodot characteristics in TMTF applications is directly applicable to more recent nanoelectronics packaging and nanopackaging applications. As a vehicle for experiments, DMTF structure is not only well-suited to the model embedded passive resistors and capacitors (Wu and Morris 2008; Lu and Wong 2008), but is also useful for the prediction of nanoelectronics/SET packaging effects, since the DMTF island sizes cover the range necessary for room temperature SET operation, which is difficult to fabricate otherwise in single island form.

3 Discontinuous thin metal film instabilities

Some of the main sources of DMTF instabilities are described below.

Thermal effects and thermo-mechanical strain: In all applications, the nanodot system will sit on some form of substrate, with electrical connections to the outside world. Conductance will show a strong negative temperature coefficient, but will also be subject to the effects of thermo-mechanical stress due to TCE mismatches. Tunneling alone gives the system a very high gauge factor, $G = (2m\Phi)^{1/2}(4\pi d/h)$, but the linear variation of G with d at low strain turns over at higher values (Boiko et al. 1972; Morris 1972d; Morris and Coutts 1977), when δE is considered, due to its predicted decrease (Fig. 2, Morris 1972d) for high eccentricity nanodots with substrate adhesion (i.e. $\theta < 180^{\circ}$). Figure 3 (Morris 1972d) shows that δE does indeed decrease in practice for positive strain. The sensitivity of electrical properties to strain suggests that vertical-tunneling devices will be more controllable than lateral-tunneling ones.

Post-deposition resistance changes: The key to DMTF formation is weak substrate adhesion, which leads to property instability due to another structural change, as nanodots drift and coalesce. Future commercial applications will require fabrication on stable nucleation sites. The oblate nanodot shape may not be the stable equilibrium form, and may change with time (Morris 1972e). Figure 4 (Morris 1975a) shows theoretical normalized resistance changes as (a) residual substrate deposited adatoms continue to migrate to the nanodot–substrate interface, adding to the nanodot mass and keeping $\theta \ll \theta_e$ (the equilibrium value, 136° for gold on glass), and (b) the nanodot eccentricity changes with surface self-diffusion away from the high curvature edge.

Air adsorption: The adsorption of air on the nanodot surface changes the work function Φ , and hence tunneling probabilities (Morris 1970; Morris and O'Krancy 1972), with a $t^{1/2}$ dependence indicative of substrate diffusion (Fig. 5, Morris 1970). Other environmental



Fig. 2 Theoretical DMTF strain effects: δE variation (Morris 1972d)

gases have similar effects (Kazmerski and Racine 1975), with H_2 absorbing into the nanodot itself (Morris et al. 1996). Clearly, any tunneling-based nanoelectronics technology will require some form of hermetic encapsulation.

Substrate ion drift and polarization: DMTF currents may change with time, due to substrate ion-drift and/or polarization (Fig. 6), and a residual voltage, which decays with time, can be measured across the film after DC application for long periods (Fig. 7, Morris 1972f). Similar effects have been observed in cermets (Kiesow et al. 2003). Such an effect would change SET turn-on voltages, for example, and means that substrate/encapsulation ionic/polarization materials properties will be of paramount importance.

Switching effects and noise: DMTFs show both N- and S-type switching (Morris 1975b, Borziak et al. 1976), but neither is understood. Voltage controlled N-type behavior can be explained in negative TCR materials by a thermal runaway model (Fig. 8, Morris 1975b) with a contact space-charge model (Wu and Morris 1998) proposed for S-type (Morris and Coutts 1977). The impact of these instability mechanisms is unclear



Fig. 3 Experimental DMTF strain effects: δE variation (Morris 1972d)



Fig. 4 DMTF R(t) model with adatom collection and surface self-diffusion (Morris 1975a)

without understanding them, but may affect the I-D chain or 2-D array SET structures, for example.

4 Reliability testing

The effects above are expected to create reliability problems for the packaging of nanoelectronic devices (Morris



Fig. 5 DMTF resistance variation upon exposure to air (Morris 1970)



Fig. 6 DMTF current variation with voltage cycling (Morris 1972f)



Fig. 7 a "Residual" voltage decay after high voltage application, and **b** high voltage current decay with time (Morris 1972f)



Fig. 8 Thermal DMTF switching (Morris 1975b)

2007). Nanodot arrays in the form of discontinuous gold films can be deposited by electron-beam evaporation on Corning 7059 glass and oxidized silicon substrates. Some films are being deposited on chromium nano-dots to evaluate the efficacy of chromium as an adhesion promoter and stabilization technique (She et al. 2006). The substrate/film combinations are "packaged" in flip-chip and wire-bond configurations, to undergo various environmental testing routines, such as mechanical stress cycling, 85/85 humidity (corrosion,) thermo-mechanical cycling, encapsulation, voltage cycling, etc., to failure, with the variations in the electrical properties of the island films monitored. The first



Fig. 9 Thermo-mechanical reliability test vehicle

reliability experiments target thermo-mechanical strain, and its effect on film resistance. The basic arrangement is shown in Fig. 9, for an oxidized silicon substrate. Electrical resistance of the DMTF is monitored during thermomechanical cycling, both with the silicon substrate coupled to the FR4 board by epoxy underfill, and decoupled from it without the underfill is removed. Quantitative comparisons of these data will permit assessment of thermo-mechanical sensitivities, which are expected to be significant given the exponential tunneling dependence.

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